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Description

Film plaster, especially for covering wounds and preventing or treating blisters, using polyurethane backing films having improved slip properties and water repellence and reduced dirt pickup propensity

The invention relates to film plasters, particularly for covering wounds and preventing or treating blisters, using backing films having improved surface properties.

Films find frequent use in plasters and first aid dressings on account of their imperviousness to water and to microbes, their conformability, and their high level of compatibility.

Accordingly, DE 43 14 834 A1 discloses a film-based dressing material covered on one side with a backing material whose size is the same as that of the film and which has at least one grip strip, and on the other side is provided with a self-adhesive layer. Essential to the invention here is that the grip strips are disposed within the peripheral boundary of the backing material. There is preferably only one grip strip on the backing material.
A plaster of this kind with a polyurethane film is available commercially under the name „Aqua Protect"® from Beiersdorf.

DE 40 26 755 A1 discloses a film-based dressing material covered on one side with a support material whose size is the same as that of the film and which has at least one grip strip, and on the other side is provided with a self-adhesive layer. In contrast to the dressing material of DE 43 14 834 C2 the grip strips for removing the backing material are disposed within the peripheral boundary of the backing material. Here too there is preferably only one grip strip on the backing material.
This plaster with a polyurethane film

Medical plasters, wound dressings, and fixings of all kinds are often subject to a phenomenon that leads to premature, unintended detachment. This phenomenon is turnup, where the product rolls back starting usually from one corner or else one edge of the plaster.

Once the plaster has come away at one point, there follows a chain reaction which leads very rapidly to complete detachment. With particular frequency, this turnup occurs with plasters worn under clothing or inside footwear. The reason is the rubbing (friction) of the clothes or shoes on the surface of the plaster. This frictional force gives rise to a dynamic shear load on the pressure-sensitive adhesive composition, which usually leads very rapidly to breaking of the bond in the edge region. After the adhesive composition has been released at one edge, the textile or leather clings to the projecting composition and, as a result of the tangentially bearing force, causes turnup and further, accelerated detachment of the whole plaster.

One way of preventing premature detachment is to increase the adhesion of the pressure-sensitive adhesive composition to the skin. This tackiness cannot, however, be increased ad infinitum, since otherwise there may be skin irritation, pain, and disturbance of the wound in the course of the intended detachment of the product.

From EP 0 409 587 A1 it is known to what extent the premature detachment of plasters is affected by the contact area A of the backing film, i.e., the area over which two sliding bodies are actually in contact.
It describes the use of thermoplastic films which during or after extrusion in the melted state are embossed by an embossing roller. Best results are obtained with a structure in which the contact area represents approximately 25% of the total area.

The use of films to form plasters produced using water repellents is not a subject of the disclosure.

According to US 5,643,187, plasters and first aid dressings combining good slip with good elasticity are obtained by means of a two-layer construction of the backing film. Low sliding friction is achieved by

layer of comparatively soft, stretchable material. Following application of the plaster, the hard, slippery side of the backing film represents the outer surface which faces the skin. A disadvantage of this method of improving the slip is an unavoidable reduction in stretchability, elasticity, and hence conformability of the backing film. In order to stretch hard films or film layers it is necessary to apply a considerably greater force, so that during use as a plaster there may be incidences of skin irritation and retarded healing owing to mechanical loads on the wound.

A method of coating medical articles, especially examination gloves and surgical gloves, is described in US 5,742,943. Use is made here of a complex mixture of different chemicals such as cationic surfactants, especially 1-hexadecylpyridine hydrochloride, acetylenediol compounds, and modified silicones. The aim of this coating is improved slip on dry or moist skin. The chemicals used for this purpose are not water repellents.

The use of elastic, slippery films to form plasters and first aid dressings produced by treating a hydrophilic polyurethane film with water repellents is not a subject of the abovementioned patents.

According to the first law of friction, the frictional force F_f is equal to the product of friction coefficient μ and normal force F_n. This coefficient is a measure of the force that must be used to move a body on a surface, μ_s denoting the static and μ_k the kinetic (sliding) friction coefficients.

The development of backings having good slip properties, i.e., low friction coefficients, is therefore a central starting point for preventing the turnup effect outlined above. Although to date, as set out in particular by Ludema (Ludema, K.C., Friction, Wear, Lubrication: a Textbook in Tribology, CRC Press, Boca Raton 1996), neither exact nor approximate methods exist for deriving friction or wear properties from fundamental principles, an inspection of the literature permits conclusions to be drawn about parameters which determine the size of μ_s and μ_k.

Static friction is governed (Blau, PJ.; Friction Science and Technology, Marcel Dekker. New York 1996) by the following

where τ_m is the shear strength,

A is the contact area, and

P* is the combination of normal force and adhesion.

Sliding friction between two bodies is determined by a range of interacting effects (Bhushan, B., Gupta, B.K.; Handbook of Tribology, McGraw-Hill New York 1991). Besides adhesion components, there occur plowing effects, roughness effects, deformation effects, and, particularly in the case of viscoelastic materials, damping effects. The relative contribution of these effects depends on the materials involved, the surface topography, the state of the sliding surfaces, and the ambient conditions.

Investigations by Bartenev (Bartenev, G.M., Lavrentev, V.V.; Friction and Wear of Polymers, Elsevier Amsterdam 1981) and Rabinowicz (Rabinowicz, E.; Friction and Wear of Materials, Wiley-Interscience, New York 1995) reveal the friction coefficient μ_k to be determined not only by contact area but also by parameters such as roughness, hardness, elasticity modulus, and surface energy of the materials.

The effect of fluoropolymers on the friction coefficient of plastics with respect to steel was investigated by Mens and de Gee (Mens, J.W.E., de Gee, A.W.J.; Friction and wear behavior of 18 polymers in contact with steel in environments of air and water, Wear **149**, 255 to 268 (1991)) using a polytetrafluorethene additive.

The table below shows the values for plastic against AISI 52100 steel at 0.1 m/s with a 500 N load without and, respectively, with the addition of PTFE.

Table 1: Effect of PTFE additive on the friction coefficients of polymer against steel

Base polymer	μ (base polymer)	μ (with 15% PTFE)
Polyamide 66	0.57	0.13
Polyoxymethylene (POM)	0.45	0.21
Polyether ether ketone (PEEK)	0.49	0.18
Polyethylene terephthalate (PET)	0.68	0.14
Polyphenylene sulfide (PPS)	0.70	0.30
Polyether imide (PEI)	0.43	0.21

It is an object of the invention to avoid the disadvantages known from the prior art and to provide a film plaster which may be self-adhesive on one side and which does not detach unintentionally from the skin side to which it has been bonded previously. Furthermore, the inventive embodiment of the film plaster reduces dirt pickup and improves water repellency. Improved water repellency in PU films is of great interest especially when polyurethane grades having very high water vapor permeabilities are used. These grades have a particularly high hydrophilicity, so that the water repellency properties of the film surface can be increased greatly by means of water repellents while the water vapor permeability of the film as a whole is not impaired.

This object is achieved by means of a film plaster as specified in the main claim. The subclaims relate to advantageous developments of the film plaster.

The present invention accordingly provides for the use of at least one hydrophilic polyurethane film particularly as a backing for medical plasters and first aid dressings, the backing being produced in particular by coating thickened polyurethane dispersions on casting papers or casting films.

The esthetics and surface structure of the films are determined by the choice of casting substrate.

[illegible] composition, the elastic polyurethane film having been

provided with fluorocarbon-, silicone- or hydrocarbon-based water repellents.

For the use of water repellents in the production of PU backing films for film plasters it is possible to minimize and tailor the surface energy within a very wide range. The surface energy of the PU film is relevant to the following product properties:

- the slip properties of the film
- dirt pickup propensity of the film plaster
- water repellency of the film.

Preferred polyurethane dispersions for producing medical plasters for covering wounds and treating or preventing blisters are polyurethane dispersions which are available, for example, from Bayer AG, Leverkusen (DE), under the names Impranil and Impraperm. By the addition of appropriate additives, these dispersions may be foamed, so that foams as well may be produced as backing. By blending different grades of Impranil and/or Impraperm and optionally preparing multi-ply layers by successive application of different foamed or unfoamed dispersions to a substrate, it is possible to produce backing materials having desired properties such as hardness, elasticity modulus, stretchability, water vapor permeability, roughness, handle, and esthetics. The films or foams, which are colorless per se, may be colored by adding commercial pigments such as Euderm (Bayer AG, Leverkusen, DE).
In the simplest embodiment, the film is composed of one layer.

To optimize the surface energy of the film, in accordance with the invention, there are two processes to choose:

Suitable additives such as, for example, the fluorine compounds Xeroderm WF (Bayer AG, Leverkusen (DE)) are added to the dispersion in an amount of up to 5% by weight. The water repellent content of the polyurethane film is preferably from 0.1 to 5% by weight, in particular from 1 to 5% by weight. Owing to the surface-active properties, this compound diffuses to the boundary face and so reduces the surface energy of the film in the finished product.

Accordingly, one preferred process for prod

5% by weight is applied to an embossed, water-resistant, silicone- or polypropylene-coated paper or film. The composite is dried.
The resulting polyurethane film is coated with a pressure-sensitive adhesive composition, which is provided, if desired, with a wound pad and an adhesive-repellent backing material, and the water-resistant, silicone- or polypropylene-coated paper or film is removed.

Owing to the high hydrophilicity of the polyurethane, the dried film may also be treated by immersing and/or spraying or coating it with aqueous dispersions of water repellents. As a result of contact with water, the polyurethane swells slightly, so that the water repellent is deposited selectively on the surface of the polyurethane and is anchored very effectively there. Subsequent drying and filming further enhances the action of the water repellent.

If the water repellent is mixed only into the top layer of the film or sprayed only onto that layer, it is exclusively the surface of the film plaster facing the skin that obtains the desired effects. The adhesion of the adhesive composition to the opposite surface is unaffected.

Accordingly, a further preferred process for producing a film plaster of the invention is as follows:
At least one polyurethane dispersion is applied to an embossed, water-resistant, silicone- or polypropylene-coated paper or film. The composite is dried.
The resulting polyurethane film is immersed completely into an aqueous dispersion containing a water repellent, in particular in a fraction of up to 40% by weight, or is sprayed with or coated with this dispersion on one or two sides, the polyurethane film is coated with a pressure-sensitive adhesive composition on one side (when treated on one side, it is appropriately the side opposite the side to be treated), the pressure-sensitive adhesive composition is provided, if desired, with a wound pad and with an adhesive-repellent backing material, and the water-resistant, silicone- or polypropylene-coated paper or film is removed.
Dispersions used with further preference contain water repellents in a fraction of up to

their chemical structure be fluorocarbon polymers, silicones or hydrocarbons.

Examples of suitable fluorocarbon polymers are available under the designations Baygard (Bayer AG, Leverkusen (DE)), Zonyl (DuPont, Bad Homburg (DE)), Stralin (Weserland Textilchemie, Hannover (DE)), and Unidyne (Daikin Chemicals, Düsseldorf (DE)) from the respective suppliers. As silicones it is possible to use, for example, Dow Corning 365 (Dow Corning, Sophia Antipolis, France) or Finish WS 60 E (Wacker, 84489 Burghausen (DE)). Examples of suitable hydrocarbon-based water repellents include Nalan GN and Nalan W (DuPont, Bad Homburg (DE)) or Perlit grades such as 40178, SE or SI-SW (Bayer AG, Leverkusen (DE)).

Combining fluorinated with nonfluorinated water repellents makes it possible to reduce the amount of fluorinated ingredient needed.

A preferred film is from about 10 to 500 μm thick, preferably from 20 to 100 μm thick, its weight accordingly being between about 15 to 600 g/m^2, preferably from 15 to 100 g/m^2, is transparent, has an ultimate tensile stress strength in the longitudinal direction of between about 2 to 100 N/cm, preferably from 5 to 40 N/cm, an elongation at break in the longitudinal direction of between about 100 to 1000%, preferably more than 450%, and a water vapor permeability of more than 500 g/m^2 in 24 h at 38°C and 95% relative humidity in accordance with DAB [German pharmacopoeia]. Where the film of the invention is composed in part of foamed layers, the thickness may be from 50 μm to 2 mm.

Pressure-sensitive adhesive (PSA) compositions used may be commercial, medical grade adhesive compositions.
The PSA composition on the polyurethane film preferably has a bond strength for steel of, for example, about 2 to 4 N/cm, it being necessary to reinforce the reverse of the test material for the measurement with an inelastic adhesive film, since the film is very stretchable. The measurement itself takes place in accordance with DAB 9.

On its optionally self-adhesive side, which subsequently faces the skin, the film plaster of the invention is usually covered over its entire width, up until the time of use, with an antiadhesive carrier material, such

method, and also stabilizes the product as a whole. The cover may be designed conventionally in one piece or, preferably, as two parts.

The film plaster may be used as it is or else a customary absorbent wound contact material or another functional material with beneficial effects on the healing of wounds or blisters may be applied centrally in appropriate width, so that the plaster can be used directly as a wound dressing. A dressing of this kind with all-round bonding is especially advantageous since it is impervious to microbes and resistant to water.

For sterilization, the product may be packaged and α-irradiated by standard techniques.

In one alternative embodiment of the film plaster, said plaster comprises an at least two-layer elastic film, the first layer being composed of an elastic polyurethane film, said polyurethane film being treated with fluorocarbon, silicone- or hydrocarbon-based water repellents, the first layer being structured, and the surface of the lower layer being coated, if desired, with a pressure-sensitive adhesive composition.

In a first preferred embodiment, between the upper layer and the lower layer there is at least one further layer which serves, inter alia, to improve the imperviousness to microbes.

In accordance with the invention, the structure of the upper layer is understood to be a raised patterning, so that the layer is not constructed flatly but instead has three-dimensional elevations and depressions. Alternatively, in one preferred embodiment, the upper layer may comprise individual discrete (i.e. separate) segments.

A film plaster of this kind may be produced to a particular effect by applying a polyurethane dispersion to an embossed, water-resistant, silicone- or polypropylene-coated paper or film so as to give a structured layer consisting in particular of individual, separate segments,
drying the composite,
applying a second and, if desired, a third polyurethane dispersion to the first.

dispersion having a solids content of up to 40 % by weight.

drying the treated film,
coating the resulting polyurethane film with a pressure-sensitive adhesive composition,
providing the pressure-sensitive adhesive composition, if desired, with a wound pad and an adhesive repellent backing material, and
removing the water-resistant, silicone- or polypropylene-coated paper or film.

The subject matter and content of the invention is to be illustrated on the basis of the following examples without wishing thereby to restrict the invention in any way whatsoever.

Example 1. Treatment with Baygard AFF

By diluting commercially available Baygard AFF (Bayer AG, Leverkusen (DE)) a 1% solution was prepared. Sample sections of a hydrophilic polyurethane film produced from Impranil DLH and Impranil DLN in a ratio of 1:1 were immersed in the solution and left therein for several minutes with gentle agitation.
The film was then removed from the bath and dried at 120°C in a drying oven, after which the water repellent was filmed at 160°C for 1 min.

Example 2. Treatment with 7-9931 (Dow Corning)

By diluting commercially available silicone-based water repellent (7-9931, Dow Corning) was diluted to a solids content of 7.5% by adding demineralized water.
Sample sections of a hydrophilic polyurethane film produced from Impranil DLH and Impranil DLN in a ratio of 1:1 were immersed in the solution and left therein for thirty minutes with gentle agitation.
The film was then removed from the bath and dried at 120°C for 10 min.

Example 3. Treatment with Nalan GN (Du Pont)

Commercially available hydrocarbon -based water repellent (Nalan GN) was diluted to a solids content of 6% using demineralized water.
Sample sections of a hydrophilic polyurethane film produced from Impranil DLH

The film was then removed from the bath and dried at 120°C for 15 min.

The table below lists hydrophilic polyurethane films of the invention treated with water repellents. The composition of the film is listed first. The second column lists the concentration of water repellent used. The friction coefficients μ, determined in accordance with DIN 53 375, and the surface energy, determined by measuring the contact angle of different liquids, are listed in the respective columns.

Table 2: Properties of polyurethane films of the invention

Film	Concentration	Surface energy [mN/m]	Friction coefficient μ
Comparative example 1	-	n.b.	1.5
1 + Xeroderm WF(1)	2%	n.b.	1.2
1 + Xeroderm WF(1)	5%	n.b.	1.2
Comparative example 2	-	30	2.3
2 + Baygard AFF(1)	1%	21	1.8
2 + Stralin TFK 3(2)	5%	15	1.7
2 + Unidyne TG 561(3)	2.5%	7	1.5
Comparative example 3	-	30	1.6
3 + Finish WS60E(4)	4%	12	0.7
3 + Silicone 365(5)	18%	31	0.9
3 + Silicone 7.9931(5)	8%	15	0.6
3 + Nalan W(6)	2.5%	11	0.8
3 + Nalan GN(6)	6%	12	1.1

(1) Bayer AG

(2) Weserland Textilchemie

(3) Daikin Chemicals

The above table shows the significance of the surface energy parameter in the production of a film-defined surface properties.

To the skilled worker it is immediately evident that these parameters are also appropriate for producing polyurethane films having desired sensation and tactility. For applications where the slip properties are less prominent than the sensation, qualities such as conformability and pleasing tactility may be improved by targeted optimization of the parameters mentioned.